Multinuclear complex formation between Ca(II) and gluconate ions in hyperalkaline solutions

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The deprotonation equlibria of the bare Gluc⁻ in hyperalkaline solutions was studied *via* potentiometric titrations, supplemented with multinuclear NMR measurements. Potentiometric titration curves obtained for Gluc⁻-containing solutions (Figure S1) display significant decrease in the cell potential relative to the Gluc⁻-free system, which is due to the deprotonation of the ligand. Modeling these measurements with the PSEQUAD computer program demonstrated, that the potential variations are consistent with a single deprotonation step associated with an alcoholic OH group of the Gluc⁻ and with the formation of $GlucOH^{2-}$ (or $Gluc_{(-H)}{}^{2-}$) No further deprotonation step (*i.e.,* formation of $Gluc(OH)_2{}^{3-}$) can be observed over the OH⁻ concentration range covered. The protonation constant of the $GlucOH^{2-}$ (for definition, see Table 1) was found to be $\log K_{011} = 0.08 \pm 0.01$, corresponding to an (acid) dissociation constant of $pK_a = 13.68 \pm 0.01$. These results agree with the semi-quantitative estimate published by Zhang *et al.*[34] ($pK_a = 13 \pm 1$), which is (to the best of our knowledge) the only approximation published in the open literature. (Note, that the autoprotolysis constant of water used in these calculations, $pK_w = [H^+][OH^-] = 13.760 \pm 0.003$, was determined from independent potentiometric titrations.)

On the ¹H-NMR (Figure S2) and ¹³C-NMR spectra (not shown), the peak positions of Gluc⁻ are significantly shifted as the pH of the solution increased. This is due to the deprotonation of an alcoholic OH group of the molecule. Under alkaline conditions a well-resolved ¹H NMR spectrum of the Gluc⁻ was recorded (Figure 1). The maximum variation on the various protons is found in the range of is $\Delta\delta = 0.25-0.35$ ppm. The fact, that the chemical shift of all the protons change on increasing NaOH concentration, and the extent of this variation is rather similar on each protons, indicate that cooperative deprotonation of the alcoholic OH groups is likely to take place, and no favored position for the deprotonation can be suggested.

The ¹³C NMR signals of the Gluc⁻ exhibited downfield shift with the raising pH of the solution. The maximum variation at the various C-atoms upon addition of NaOH, $\Delta\delta$ was found to be in the range of 0.20−2.45 ppm. This made it possible to use ¹³C-NMR measurements as an independent means for the determination of the deprotonation constant of Gluc⁻. The δ *vs.* log[OH⁻] plots were found to be

saturation curves (not shown) and the proton dissociation constant of the $Gluc^-$ extracted from them was found to be $\log K_{011} = -0.09 \pm 0.05$, which is in reasonable agreement with the value obtained from potentiometry.
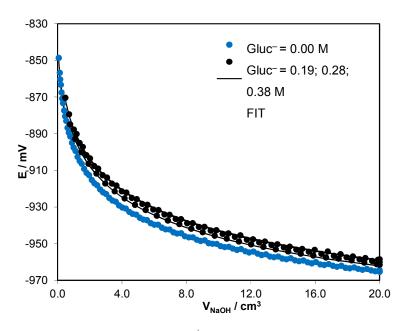

Figure S1. Potentiometric titration curves of the H^+/$Gluc^-$ systems. Dots represent observed EMF values, solid lines were fitted on the basis of the model discussed in the text. (Titrant: 1.00 M NaOH)
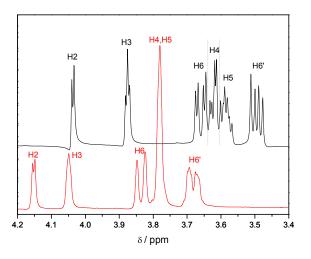

Figure S2. The ^1H NMR spectra of solutions with $[NaGluc]_T = 0.200$ M at neutral pH (red) and in 1.00 M NaOH medium (black) with peak assignments
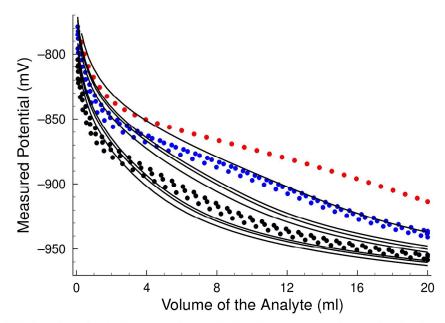
Figure S3. The fitted H_2/Pt–electrode potentiometric titration curves when only the formation of the two mononuclear (*i.e.* CaGluc$^+$ and [CaGlucOH]^0) is assumed. (Titrant: 1.03 M NaOH; T = 25.00 °C)
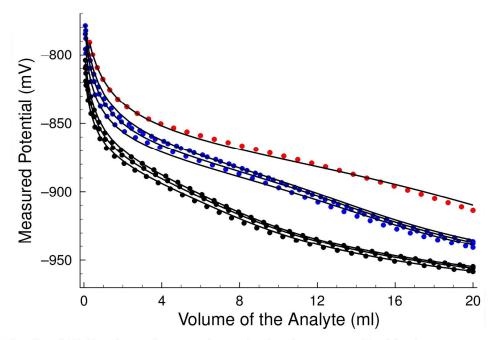

Figure S4. The fitted H_2/Pt–electrode potentiometric titration curves. Beside the two mononuclear (*i.e.* CaGluc$^+$ and [CaGlucOH]^0) complexes, the [Ca$_2$Gluc(OH)$_3$]^0 binuclear complex was included in the model.
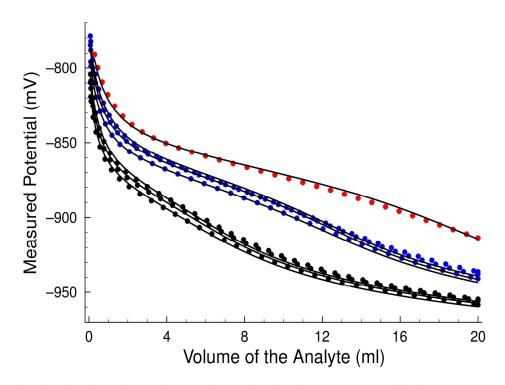
Figure S5. The fitted H_2/Pt–electrode potentiometric titration curves. Beside the two mononuclear (*i.e.* CaGluc$^+$ and [CaGlucOH]^0) complexes, the [Ca$_3$Gluc$_2$(OH)$_4$]^0 trinuclear complex was included in the model.
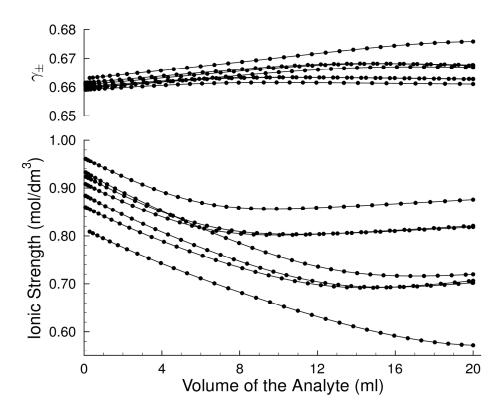

Figure S6. Change in the ionic strength (lower part) and in the mean activity coefficient (upper part) during the potentiometric titrations. The ionic strength was calculated by the finally accepted equilibrium

model while the $\gamma_{\pm}$ values were computed based on Refs S1 and S2. The largest change is 41 % for the ionic strength and the change of the corresponding mean activity coefficient does not exceed 2.0 %.
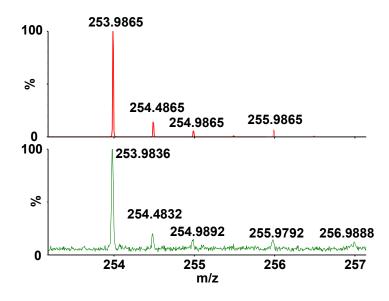

Figure S7. The ESI−MS trace of a solution containing 0.020 M Gluc⁻ and 0.020 M Ca^{2+} in 0.102 M NaOH medium; positive ion mode. The peak at 253.98 m/z value refers to the $[Ca_3Gluc_2(OH)_4]^0$ trinuclear complex as a $[Ca_3Gluc_2H_{-2}]^{2+}$ species.

Conductometric titrations: The effect of dilution adding water to calcium chloride and sodium gluconate solutions can be seen in Figure S7 and are marked with black squares. In the case of solution containing both compounds, the total conductance is equal to the conductance of $CaCl_2$. Though, the relation between conductivity and concentration is not linear (about > 0.01 M), this property and the effect of dilution can't explain the decrease in the conductance. So this change has to be due to the formation of CaGluc⁺ (which has surely very little molar conductivity). This effect is much more significant when the titrant is NaOH. In contempt of the high molar conductivity, the conductance is broadly constant from V = 0 to 12 cm^3. This phenomenon is due to the complexes containing OH⁻ ions. The large extent of complex formation is because of the high concentration of gluconate.
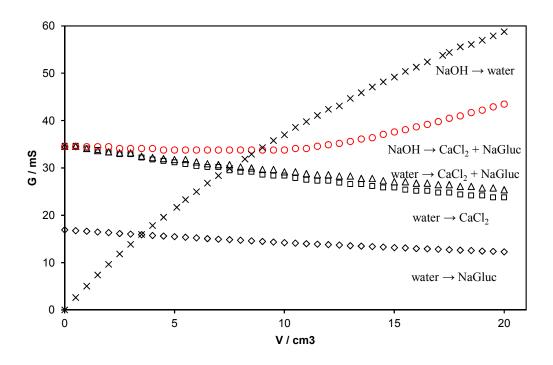
Figure S8. Conductometric titrations in the $Ca^{2+}/Gluc^-$ system. $[Ca^{2+}]_{T,0} = 0.2407$ M, $[Gluc^-]_{T,0} = 0.4125$ M, $c_{NaOH} = 0.7739$ M. The titrands are shown on the left side of the arrow.

The equivalence point is 11.8 cm^3 ($V_0 = 35$ cm^3). From calculated data, ~90% of the calcium ions are bonded in complexes when $[Ca^{2+}]_T = 0.1800$ M, $[Gluc^-]_T = 0.3085$ M and $[OH^-]_T = 0.1951$ M. The calculated eq. point is 13.07 cm^3. This little difference might be caused by the different ionic strength and total concentrations (as maintaining the constant ionic strength in this system is impossible), and the fact that complex formation is never a fully quantitative reaction. The similarity between the two values obtained by conductometry and potentiometry gives back the stoichiometry of the complexes.

Table S1. The structural parameters calculated from the EXAFS spectra of the solution containing 0.200 M CaCl$_2$ and 0.500 M NaGluc at pH~13; N: coordination number; R: bond length; σ^2: Debye−Waller factor

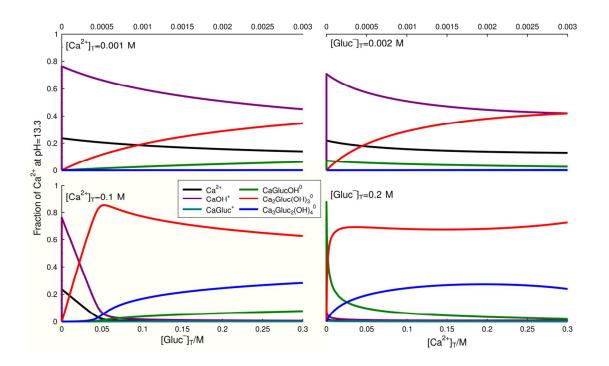|	N	R / pm	σ^2
Ca − O	6.28	239	0.00785
Ca − Ca	1.00	365	0.00136

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Figure S9 Calculated distrubutions at variable Ca:Gluc ratios and at pH_{calc}=13.3 to show the significance of different Ca-containig compounds in different concentration ranges. For the calculations, conditional stability constants obtained at 1 M NaClé ionic strength were used. The species having constant total concentration is indicated in the top left corner of the subfigures.

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